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16. ABSTRACT

This paper ~~will~~ present an overview of the research activities conducted by the U. S. EPA Remedial Action Program during the period of 1984 through September 1987. Special emphasis ~~will~~ be placed on in-situ and on-site technologies which utilize chemical techniques to minimize the migration of contaminants from uncontrolled hazardous waste sites. The subjects ~~to be~~ discussed include: delivery and recovery technologies; chemical treatment of metals; chemical treatment of organics and inorganics; and immobilization by chemical means.

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Introduction

This paper will present an overview of the research activities conducted by the U.S. EPA Remedial Action Program during the period 1984 through September, 1987. Special emphasis will be placed on in-situ and on-site technologies which utilize chemical techniques to minimize the migration of contaminants from uncontrolled hazardous waste sites.

Many existing technologies, such as those used in the construction industry, wastewater treatment and hazardous waste fixation/treatment can be applied to uncontrolled waste sites. However, their application must be tested, cost and effectiveness determined, and limitations understood, so that they may be effectively and economically utilized. The three major problems at uncontrolled hazardous waste sites include the waste itself, contaminated ground and contaminated groundwater. Traditionally, remedial actions have involved removal and burial in a secure landfill or isolation at the site. There are many obvious drawbacks to this approach that make in-situ and on-site technologies more desirable.

In order to develop an effective remedial action scenario for uncontrolled hazardous waste sites, it is necessary to effectively integrate physical, biological, and chemical methods in the majority of cases, and it is the experience gained through pilot and field scale demonstrations that tells us how this can best be accomplished. Once the migration of contaminants from a site has been stopped via various engineering techniques, chemical and biological methods used separately, or in concert, can be used to minimize the resulting environmental impacts. Chemical treatment of contaminated soils entails the reaction of pollutants with reagents, resulting in products which are less toxic, or which become immobilized, especially in-situ; and is dictated by site geology and hydrology, soil characteristics and waste characteristics. Most hazardous waste disposal sites contain a mix of contaminants, as well as soil grain sizes and types. The compounding multiplicity of critical factors encountered at hazardous waste sites makes it extremely complicated to predict workable economic solutions and accounts for the limited application, to date, of in-situ and on-site treatment techniques.

Concern over the long-term reliability of land-based disposal practices has prompted elected and regulatory officials to develop more stringent controls on its use. Superfund officials are also developing program policies to encourage the use of waste management techniques that are not dependent on land disposal practices.

In-situ treatment can be effective in eliminating or reducing the hazard to acceptable levels. In-situ treatment of contaminated soils must be based on an understanding of factors and processes that determine the behavior of chemicals in soil systems. Specifically, an evaluation

of chemical properties, biochemical processes, and environmental factors influencing the behavior and fate of chemicals is required. The goals of in-situ management include treating contaminated soils until acceptable levels of hazardous materials are achieved so that ground water and surface water resources are protected. In those cases where in-situ treatment is determined to be a feasible approach, it will usually be implemented as a part of an overall remedial action scenario involving the use of other methodologies (e.g., containment) in parallel.

Definition of In-Situ Treatment

The term in-situ treatment of contaminated ground means that the treatment is applied without excavation of the material to be treated, irrespective of whether the waste is excavated as a total mass or removed in increments, and irrespective of whether the treated product is replaced or otherwise disposed of. Most treatment systems have in common the need to inject fluids into the ground in one way or another.

Classifications of Treatment Methods

The potential methods of in-situ treatment can be classified in terms of their objectives:

1. To render the contamination harmless. This embraces such processes as microbial or chemical treatment to destroy the contaminants and ground leaching to remove them physically.

2. "Stabilization" in which the hazardous contaminants are rendered insoluble or otherwise immobile, or their hazardous characteristics (e.g., toxicity or combustibility) are neutralized.

3. "Solidification" involving the conversion of the contaminated ground into a solid mass.

Treatment Technologies

In general the treatment technologies are adaptations or engineered processes to enhance natural methods for the reduction of the concentration of hazardous compounds or the reduction of the toxicity effect that the compounds may exhibit. Volatilization of organics or vacuum extraction of volatile compounds; soil washing with water, chelates, or surfactants may remove soluble inorganic or organic hazardous materials for subsequent treatment on or off-site. Chemical neutralization, oxidation, or reduction can destroy specific hazardous substances, precipitation of metals with lime or sulfide can immobilize the metals and reduce toxicity; solidification either with cement grouts, asphalts, or by soil vitrification, can also immobilize inorganic and organic compounds and reduce hazardous effects.

Delivery and Recovery Technologies

Delivery and recovery methods are critical for successful accomplishment

of soil washing/flushing, chemical treatment, and biological treatment at the in-situ sites. The available delivery methods are grouped into two generic categories: gravity and forced. In gravity applications, the flushing, or reactant, solution is applied directly over the waste deposit or delivered through the surrounding soil media to the waste deposit. After the solution percolates through the waste deposit, it enters the ground water. In forced methods, the flushing or reactant solution is directly injected into the waste deposit or surrounding soil medium through pipes by means of an applied pressure. The solution, after passing through the waste deposit, enters the ground water for subsequent recovery. A number of gravity delivery methods are available for selection including: flooding, ponding, surface spraying, ditch, infiltration galley and infiltration bed.

The forced delivery method would be cost effective for a waste deposit and surrounding soil medium having a low permeability and low infiltration rate which precludes the delivery of treatment solution by natural gravity. Such systems would typically be comprised of an injection pipe (open end or slotted) and pump.

Available recovery technologies can be categorized as gravity and forced. Gravity recovery depends upon interception of the ground water, downgradient from the waste deposit. After applied, treatment solutions pass through the waste deposit and enter the ground water, the resultant fluid is collected in an interceptor system (i.e., open ditch or buried drain) by simple gravity flow. Forced recovery systems utilize well points, deep wells or vacuum well points located in the ground water downgradient of the waste deposit to remove spent solutions by mechanical means.

There are some potential augmenting technologies available for improving the effectiveness of chemical treatment methods such as: electro-kinetics, hydrofracturing, horizontal wells/drilling, pulsed pumping/injection, colloidal gas aphrons, and ground freezing. Although these augmenting methods are not chemical treatment in nature, they need to be considered and the U. S. EPA is currently investigating them.

With respect to electro-kinetics, a number of electro-chemical effects may result when a voltage difference is applied across a saturated subsurface zone. Such electro-chemical effects include: ion diffusion, ion exchange, development of osmotic and pH gradients, desiccation due to heat generation at the electrodes, mineral decomposition, precipitation of salt and secondary minerals, electrolysis, hydrolysis, oxidation, reduction, physical and chemical adsorption and soil fabric change. These effects, about which considerably less is known than about the electro-kinetic flow phenomena, may, in fact, be the most important in the application of electro-kinetic treatments to hazardous waste sites.

Electro-kinetics might conceivably be used in five general ways for hazardous waste site remediation; namely, 1) concentration and dewatering of waste sludges, slimes, dredge spoils, etc., 2) extraction of pollutants from the soil and groundwater, 3) creation of hydraulic flow barriers,

4) injection of grouts or clean-up chemicals, and 5) improvement in the effective permeability of a soil mass (Mitchell, J.K., 1986).

Three other promising innovative techniques are hydrofracturing, horizontal wells/drilling, and pulsed pumping and injection. In the oil industry, production is stimulated by over pressuring wells and hydrofracturing the reservoir strata to effect an increase in permeability. Although application of hydrofracturing to enhance recovery of contaminants from soil (and delivery of in-situ treatment agents) shows promise, evaluating those applications remains in its infancy. The focus of the hydrofracturing research is to develop techniques to predict and influence the shape, location, and orientation of hydrofractures formed in soils (Ammon, D., 1987).

Although horizontal wells/drilling technology has been available for many years, only recently have techniques been developed to place multiple horizontal wells at precise levels from one vertical well. Since soil strata tend to have planar orientations, there are obvious intrinsic geometric advantages to horizontal wells as delivery and recovery systems. For example, horizontal wells can be placed directly in formations with different hydraulic properties, allowing independent and very specific injection and drainage; wells could be placed directly in the leachate plume or under the contaminated soils/waste to allow removal before any mixing occurs with ground water; and injection of stabilization agents could be directed within or beneath a waste deposit. The focus of horizontal well research is to evaluate these techniques with a pilot-scale demonstration (Ammon, D., 1987).

Pulsed pumping/injection offers a method for optimizing the efficiency of the delivery and recovery systems and greatly reducing the amount of in-situ treatment agents used and concentrating the recovery systems effluent (and saving treatment and operation costs). The focus of this research is to develop design information on the actual site engineering aspects of pulsed pumping and injection techniques and to test these techniques with a field study at a Superfund site. (Ammon, D., 1987.)

The objectives of the Aphron study are to evaluate in the pilot plant the use of Colloidal Gas Aphrons (CGA) (50-60% dispersion of 25-50 micron bubbles in water) for: 1) in-situ biodegradation of hazardous organics in the saturated zone and 2) stripping of dissolved organics from the saturated zone. Initially, the approach will be to characterize the movement and retention of Colloidal Gas Aphrons in a two-dimension vertical test slice (7 ft. x 7 ft. x 5 in. deep). These results will be compared to the movement of air (oxygen) when provided by saturated water and 100 ppm hydrogen peroxide (free oxygen) operating in an injection/recovery mode. Depending on the outcome, the CGA's incorporated as a one-step treatment formulation will be used for treating an insoluble hazardous release (hexadecane surrogate) or a contaminated flowing ground water (xylene surrogate). In a separate activity, CGA's will be tested for stripping of TCE from a solubilized contaminated ground water in-situ at the laboratory and pilot scale, and compared to stripping with direct air injection. (Lewis, R, 1987.)

Artificial ground freezing has potential to be used as an in-situ technique to facilitate decontamination of uncontrolled hazardous waste sites. Several aspects of soil freezing are being investigated. In the earliest research, a zone of high concentration of chemicals was observed to occur ahead of the freezing front when slow freezing rates were utilized to freeze contaminated soil. In other words, contaminants moved with the freezing front as it advanced through the soil. In the more current research effort, a controlled freezing rate and an engineered design is being used to force contaminants present in a large contaminated area (volume, actually) to move toward a selected mass of soil that is limited in size. By forcing and directing contaminants from a large zone to a small zone, the large zone would be decontaminated, and a small zone containing highly concentrated contaminants would result. Removal or treatment of the contaminated soil would thus be facilitated because the volume of soil needing removal or final treatment would be greatly reduced. Final treatment (by some method other than freezing) of a small volume of soil would be more economical than treating the entire soil mass present at a site. A second aspect of soil freezing is that freezing and thawing of soil changes the permeability of the soil, usually resulting in an increase, therefore improving the potential success of effective delivery and recovery systems. A third aspect of soil freezing technology is that research to date has indicated that the process of freezing and thawing greatly increases the volatilization of volatile organics from the soil. So, again, soil freezing technology might be useful to enhance removal of contaminants from soil by volatilization. (Iskandar, I. K., Houthoofd, J. M., 1986.)

Chemical Treatment of Metals

Chemical treatment of metals is best applied on-site after separating the soil into its various grain sizes, such as sand-gravel-silt-clay, etc., then treating each fraction individually. For the sand and gravel portions, the chemical contaminants are not absorbed, they adhere to the surface and are easily removed. On the other hand, for silts and clays, the contaminants get bound into the material ionically and are very difficult to treat with present methods. The metals in the silty-clay portion should be separated and then stabilized. Now, at least until further research is done, immobilization techniques should be applied to prevent leaching of contaminants.

Dilute solutions of acids have been widely used in industrial processes to extract metal ions. Solutions of sulfuric, hydrochloric, nitric, phosphoric, and carbonic acid are used in industrial applications to dissolve basic metal salts (hydroxides, oxides, and carbonates). However, because of the toxicity of many acids, it is desirable to use weak acids for in-situ treatment. Sodium dihydrogen phosphate (NaH_2PO_4) and acetic acid (CH_3COOH) have low toxicity and are reasonably stable. A stronger dilute acid such as sulfuric acid would be used if the soil contained sufficient alkalinity to neutralize it. Acidic solutions may also serve to flush some basic organics such as amines, ethers, and anilines.

Complexing and chelating agents may also find use in a solution

used routinely in municipal wastewater treatment to control various factors of biological treatment, and is also used in industrial waste treatment to detoxify cyanide and various organic pollutants. It is commercially available in aqueous solutions of several concentrations and is miscible in water at all concentrations. It has been delivered successfully in dilute solutions to the subsurface as an oxygen source in a bioreclamation project (Raymond, Jamison, and Hudson, 1984). Several suppliers have developed a line of hydrogen peroxide solutions specifically designed for reclamation purposes.

Chemical reduction is the process by which the oxidation state of a compound is reduced. Reducing agents are electron donors, with reduction accomplished by the addition of electrons to the atom.

Chemical reduction does not appear as promising as oxidation for the treatment of organics. Although researchers have demonstrated reductive dehalogenation of a variety of chlorinated organics and reduction of unsaturated aromatics and aliphatics in laboratory studies using catalyzed metal powders, the treatment reagents are costly and the effectiveness of chemical reduction in soils remains to be demonstrated.

Chemical reduction does, however, appear promising for treatment of chromium and selenium in soils. The in-situ reduction of hexavalent to divalent chromium has been accomplished in Arizona well water using minute quantities of reducing agent. (Srivastva and Haji-Djafari, 1983).

In Japan the Bureau of Environmental Protection of the Tokyo Metropolitan Government identified a number of sites that had become contaminated as the result of the disposal of chromite roast residues from the manufacturing of sodium bichromate. The remedial actions consisted of excavation of the primary contaminated areas and treatment of the secondary contaminated areas with the reducing agent, ferrous sulphate. The soluble, hexavalent chromium was thereby reduced to the insoluble trivalent chromium. (Smith, M. A. , 1985.)

There are a number of disadvantages with the use of oxidizing and reducing agents which limit their use at hazardous waste sites. The treatment compounds are non-specific and this may result in degradation of non-targeted compounds. There is the potential, particularly with oxidation, for the formation of more toxic or more mobile degradation products. Also, the introduction of these chemicals into the ground water system may create a pollution problem in itself. As with soil flushing, uncertainty exists with respect to obtaining adequate contact with the contaminants in the plume.

The U. S. EPA has tested the use of an aqueous nonionic surfactant pair for cleaning soil spiked with PCBs, petroleum hydrocarbons and chlorophenols which was developed through bench scale shaker table tests and larger scale soil column tests. The extent of contaminant removal from the soil was 92 percent for the PCBs, using 0.75 percent each of Adsee® 799 (Witco Chemical) and Hyonic® NP-90 (Diamond Shamrock) in water. For the petroleum hydrocarbons, the removal with a 2 percent aqueous solution

mining removal system for heavy metals. Some commonly employed substances are citric acid, ethylenediaminetetracetic acid (EDTA), and diethylene-triaminepentacetic acid (DTPA). (Rogoshewski and Corstea, 1980.) Chelating agents used for in-situ treatment must result in a stable metal-chelate complex which is resistant to decomposition and degradation.

Another possibility for mobilizing metals which are strongly adsorbed to manganese and iron oxides in soils is to reduce the metal oxides which results in release of the heavy metal into solution. Chelating agents, or acids, can then be used to keep the metals in solution. Treatment agents which may be suitable for this purpose include hydroxylamine together with an acid, or sodium dithionite/citrate.

Chemical Treatment of Organics and Inorganics

In-situ treatment techniques discussed here are those which serve to destroy, degrade, or otherwise reduce the toxicity of contaminants and include neutralization, hydrolysis, oxidation/reduction, enzymatic degradation, and permeable treatment beds.

Neutralization involves injecting dilute acids or bases into the ground water to adjust the pH. This pH adjustment can serve as pretreatment prior to in-situ biodegradation, oxidation, or reduction to optimize the pH range. It can be used to neutralize acidic or basic plumes that need no other treatment, or to neutralize ground water following another treatment. It can also be used during oxidation, reduction, or precipitation to prevent the formation of toxic gases including hydrogen sulfide and hydrogen cyanide.

The pH adjustment can also be used to increase the hydrolysis rate of certain organics. Of the parameters which affect the rate of hydrolysis (temperature, solvent composition, catalysis, and pH), pH adjustment has the greatest potential. The rate of hydrolysis can be increased up to one order of magnitude for a change of one standard unit in pH (USEPA, 1985). Classes of compounds with potential for in-situ degradation by hydrolysis include:

- Esters
- Amides
- Carbamates
- Phosphoric and phosphonic acid esters
- Pesticides.

Because a hydrolysis product may be more toxic than the original compound, the pathways for reactions must be determined to ensure toxic products are not produced. USEPA (1985) has a more thorough discussion of this technology.

Oxidation and reduction reactions serve to alter the oxidation state of a compound through loss or gain of electrons, respectively. Such reactions can detoxify, precipitate, or solubilize metals, and decompose, detoxify, or solubilize organics. Oxidation may render organics more

amenable to biological degradation. As with many of these chemical treatment technologies, oxidation/reduction techniques are standard waste water treatment approaches, but their application as in-situ treatment technologies is largely conceptual.

Oxidation of inorganics in soils, for all practical purposes, has been limited to oxidation of arsenic and possibly some lead compounds. The in-situ oxidation of arsenic compounds with potassium permanganate ($KMnO_4$) has been used to successfully reduce the arsenic concentrations in ground water in the vicinity of a zinc ore smelter near Cologne, Germany (Stief, 1984). 64,000 lb. of $KMnO_4$ were injected into 17 wells and piezometer wells resulting in an average decrease in arsenic ground water concentrations from 13.6 mg/l to 0.06 mg/l from 1975 to 1977. In 1979, however, an increase indicated that the mixing of ground water and KMnO4 had not been thorough.

Of the numerous oxidizing agents available, three have been considered potentially useful in the in-situ detoxification of organics, ground water, and soils contaminated with organics: hydrogen peroxide, ozone, and hypochlorites (USEPA, 1985). Each can react with a broad range of organics and could potentially oxidize a number of different organic contaminants in a hazardous waste site. Selection of the appropriate oxidizing agent is dependent in part upon the substance or substances to be detoxified, but also upon the feasibility of delivery and environmental safety. There are some compounds that will not react with hydrogen peroxide but will react with ozone or hypochlorite.

Ozone gas is a very strong oxidizing agent that is very unstable and extremely reactive. It cannot be shipped or stored; therefore it must be generated on-site prior to application. Ozone rapidly decomposes and its half-life in ground water is only 18 minutes (USEPA, 1985). Ozone is used in the treatment of drinking water, municipal wastewater, and industrial waste, and has been used in the treatment of contaminated soils and ground water at the Karlsruhe site in Germany (Rice, 1984). A well field which served as a drinking water supply for over 500,000 people was rejuvenated. Ozone oxidation with ultraviolet irradiation has been used to successfully reduce concentrations of benzene, phenols, and trichloroethylene in lake water.

Hypochlorite, generally available as potassium, calcium, or sodium hypochlorite (bleach) is also used in the treatment of drinking water, municipal wastewater, and industrial waste. Hypochlorites have never been used in the treatment of contaminated ground water or soils. Tolman et al., (1978) has described the conceptual design and in-situ detoxification of cyanide with sodium hypochlorite. The reaction of many organics with hypochlorite results in the formation of chlorinated organics which can be equally or more toxic than the original contaminant. The formation of lower molecular weight chlorinated organics, (e.g., trihalomethanes) in drinking water from hypochlorite treatment for disinfection purposes has become a major concern of the drinking water industry.

Hydrogen peroxide (H_2O_2), a moderate strength chemical oxidant, is

of each surfactant was 93 percent. These removals are orders of magnitude greater than obtained with just water washing and represent a significant improvement over existing in-situ cleanup technology. (Ellis, W. D., Payne, J. R., McNabb, G. D., Tafuri, A. N., 1985.)

Surfactants can be mutagenic and this can be a problem. The use of surfactants is a purposeful attempt to put contaminants into solution. Large volumes of solution are also created and these are very difficult to treat. These are major factors that need to be considered when making a decision on whether or not to use surfactants.

Chemical reagents prepared from polyethylene glycols and potassium hydroxide (KPEGs) have been demonstrated under mild conditions (25°-140°C) to dehalogenate PCBs, PCDDs, and PCDFs with laboratory destruction efficiencies exceeding 99.9999%. The reaction mechanism is nucleophilic substitution at an aromatic carbon.

Bench scale studies have already established conditions for PCB destruction to less than 1 ppm and polychlorinated dibenzo-p-dioxins (PCDDs, and polychlorinated dibenzofurans (PCDFs) to less than 1 ppb. Toxicological tests have established that arylpolyglycol by-products from KPEG reactions are non-toxic. The non-toxic property of the by-products may allow for delisting and on-site disposal of treated arylhalide contaminated materials. In July and August 1986, a 2700 gallon KPEG was used in Butte, Montana on a wood preserving site and in Kent, Washington, on a waste disposal site to successfully destroy PCDDs and PCDFs (120 ppb - 200 ppm) in 17,000 gallons of liquid waste to non-detectable levels. A prototype reactor designed to treat both liquids and solids will be tested in 1987 on selected Superfund and Department of Defense sites. These field studies will validate or establish conditions in the prototype reactor for destruction of PCBs, PCDDs, and PCDFs to acceptable levels required by the pertinent regulations.

Halogenated organics are frequently identified as constituents of concern in hazardous waste spills and disposal. The halogenated solvents as a group are generally toxic, resistant to degradation, and difficult to dispose of in an environmentally acceptable manner. U. S. EPA scientists (Charles J. Rogers and Alfred Kornel, 1987) will soon receive a patent on a novel chemical destruction technique based on catalytic dehydrohalogenation. The catalytic reaction (low molecular weight glycols and base) has been demonstrated to destroy a number of halogenated compounds including carbon tetrachloride, chloroethane, ethylene dibromide, and chloropicrin.

Another experimental process is based on special properties of water when it is above the thermodynamic critical condition of 374°C and 3200 psi. In this state, oxygen and organic materials are completely solubilized in water, so that the compounds exhibit the same density in the liquid and vapor phases. This process utilizes water at a temperature and pressure above its critical point (so called "super-critical" water with temperature above 374°C and pressure over 3200 psi) to break down organic substances to carbon dioxide and water. Some inorganic compounds such as halogens, phosphorus, and sulphur may be decomposed by a similar

process and converted from highly toxic complex forms to weak acids. This supercritical treatment method is a separation technique. Supercritical water is not the only approach, supercritical CO_2 and other materials are currently being studied at Louisiana State University (Knoph, F. C., 1987) and the University of Illinois (Eckert, C., 1987). There is also ongoing research using catalysts for reducing the temperatures and pressures of this supercritical technique.

Immobilization by Chemical Means

Immobilization methods are designed to render contaminants insoluble and prevent leaching of the contaminants from the soil matrix and their movement from the area of contamination. Little is currently known about the effectiveness and reliability of immobilization techniques (Truett, Holberger, and Sanning, 1982).

Immobilization methods which are currently being investigated include: precipitation, chelation, and polymerization.

Precipitation is the most promising method for immobilizing dissolved metals such as lead, cadmium, zinc, and iron. Some forms of arsenic, chromium, mercury, and some organic fatty acids can also be treated by precipitation (Huibregtse and Kastman, 1979). All of the divalent metal cations can be precipitated using sulfide, phosphate, hydroxide, or carbonate. However, the solubility product and the stability of the metal complexes vary. Because of the low solubility product of sulfides and the stability of the metal sulfide over a broad pH range, sulfide precipitation looks most promising. The remaining anions decrease in effectiveness in the following order: phosphate > hydroxide > carbonate. Metal carbonates and hydroxides are stable only over a narrow pH range and the optimum pH range varies for different metals. Precipitation of the metal as the metal phosphate may require very high concentrations of orthophosphate, since calcium and other naturally occurring soil cations are present in high concentrations and will precipitate first.

Sodium sulfide used in conjunction with sodium hydroxide has shown widespread applicability for precipitation of metals. Precipitation takes place at a neutral or slightly alkaline pH. Resolubilization of sulfides is low. Addition of sodium hydroxide minimizes the formation of hydrogen sulfide gas by assuring an alkaline pH. Experiments with sulfide precipitation of zinc indicate that a high residual of unreacted sulfide may remain in solution.

As with other in-situ techniques, precipitation is most applicable to sites with sand or coarse silt strata. Disadvantages include the injection of a potential ground water pollutant; the potential for formation of toxic gases (in the case of sulfide treatment); the potential for clogging soil pore space; and the possibility of precipitate resolubilization.

The use of chelating agents may also be a very effective means of immobilizing metals although considerable research is needed in this

area. Depending upon the specific chelating agent, stable metal chelates may be highly mobile or may be strongly sorbed to the soil. Tetran is an example of a chelating agent which is strongly sorbed to clay in soils (USEPA, 1984a).

A third method for immobilizing metals applies specifically to chromium and selenium. These metals can be present in the highly mobile, hexavalent state but can be reduced to less mobile Cr (III) and Se (IV) by addition of ferrous sulfate. Arsenic exists in soils as either arsenate, As (V), or as arsenite, As (III), the more toxic and soluble form. Arsenic can be effectively immobilized by oxidizing As (III) to As (IV) and treating the As (IV) with ferrous sulfate to form highly insoluble Fe_2AsO_4.

Polymerization involves injection of a catalyst into a ground water plume to cause polymerization of an organic monomer (e.g., styrene, vinyl chloride, isoprene, methyl methacrylate, and acrylonitrile). The polymerization reaction transforms the once fluid substance into a gel-like, non-mobile mass. In-situ polymerization is a technique most suited for ground water cleanup following land spills or underground leaks of pure monomer. Applications for uncontrolled hazardous waste sites are very limited. Major disadvantages include very limited application and difficulty of initiating sufficient contact of the catalyst with the dispersed monomer (Huibregtse and Kastman, 1979). In-situ polymerization was successfully performed to remedy an acrylate monomer leak, in which 4,200 gallons of acrylate monomer leaked from a corroded underground pipeline into a glacial sand and gravel layer. Soil borings indicated that as much as 90 percent of the monomer had been polymerized by injection of a catalyst, activator, and wetting agent.

Summary

With the recent passage of the Superfund Amendments and Reauthorization Act of 1986, the U. S. EPA has proposed to restrict 12 classes of hazardous substances for land disposal at hazardous waste facilities, starting in July 1987. The substances include liquid hazardous wastes containing cyanides, metals, polychlorinated biphenyls (PCBs), corrosive wastes, and both liquid and solid hazardous waste containing halogenated organic compounds (HOCs). Halogenated organic compounds are a wide-ranging group of commonly used organic chemicals which include the substances chlorine, bromine and fluorine. Many of the compounds can cause cancer, birth and genetic defects, or damage to the liver, lungs, and kidneys. The U. S. EPA has also prohibited the land disposal of two categories of hazardous wastes, concentrated spent solvents and dioxins.

In light of the land disposal restrictions, many hazardous substances will have to be treated and reduced to acceptable levels of toxicity before being disposed of in waste facilities on land. The delivery and recovery techologies, the chemical treatment techniques and methods, and immobilization technologies by chemical means discussed in this paper, represent an overview of the remedial action research that is being conducted by the U. S. EPA's Hazardous Waste Engineering Research Laboratory

and others in cleaning up hazardous wastes at uncontrolled Superfund sites. The Hazardous Waste Engineering Research Laboratory is providing Best Demonstrated Available Technology (BDAT) research that will provide technical information related to the latest laws banning land disposal of hazardous wastes. The Laboratory is the technical research organization responsible for Best Demonstrated Available Technologies (BDAT).

In regard to recommendations, there is a strong need for a multiple data base established in multi-media technical areas. A single research project is not adequate to get this data base. Research efforts need to be coordinated on a multiple agency, multiple individual level, to overcome the enormously complicated, complex problem of uncontrolled hazardous waste sites.

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